## REMARKS

Claim 1 has been amended to incorporate the recitations of claims 6 and 7, and claims 6 and 7 have been canceled. Claim 1 has also been amended to include recitations from claim 16. Claim 16 has been amended so that it is in independent form. Claims 18 and 19 have been amended to depend from claim 16. Claims 26 and 27 have been added based on the disclosure at, e.g., page 28 in the specification.

Entry of the above amendment is respectfully requested.

**Interview Held February 27, 2008**

Applicants thank the Examiner for the personal interview held with their representative on February 27, 2008. Applicants believe that the interview was helpful in advancing the prosecution of this application, and have conducted additional experimentation as shown in the Declaration submitted herewith and made claim amendments as a result of the interview. A Statement of Substance of Interview is being submitted herewith.

**Information Disclosure Statement**

An Information Disclosure Statement is being submitted herewith. The Examiner is respectfully requested to consider the disclosed information and return an initialed PTO/SB/08 form with the next communication from the PTO.

**Obviousness Rejection**

On page 2 of the Office Action, in paragraph 2, claims 1-25 are rejected under 35 U.S.C. 103(a) as being unpatentable over Saito et al. US 6,436,567.

In response, Applicants note that Saito et al. describes in column 3, lines 20-29 that "[T]he rubbers can be ... butadiene rubber ... [B]y the use of such a rubber, the resulting separator can have higher impact resistance." From this description, it is inferred that the butadiene rubber was not used for preparing a hard product, i.e., the cured product having a Tg of 160°C or more and a bending strength of 30 MPa or more in accordance with JIS K 6911 as defined in the present invention. In order to enhance impact resistance of a product, normally butadiene rubber, which is in a rubber-like state at room temperature, is formulated into the product. 1,2-polybutadiene is a polymer which has a partial crystallinity, and the crystalline parts acts as cross-linked points, thereby exhibiting a rubber-like property. However, 1,2-polybutadiene, if it has been cured as a result of cross-linking the carbon-carbon double bonds in the side chain, becomes a cured product (having a Tg of 160°C or more and a bending strength of 30 MPa or more) having a three-dimensional network structure and does not exhibit a rubber-like property anymore. For the Examiner's reference, Applicants submit herewith a copy of POLYMERIC MATERIALS ENCYCLOPEDIA, edited by JOSEPH C. SALAMONE, (1996) Vol. 8, p. 5657-5663, which discusses properties of a variety of non-cured polybutadienes, and a copy of the Nisso-PB product catalog at URL (http://www.nippon-soda.co.jp/pb-j/products/index4.html).

In further regard to the issue of impact resistance, Applicants submit herewith a copy of Polymer Testing 15 (1996) 363-380, which describes a correlation between ethylene propylene rubber (EPR; ethylene-propylene copolymer, which is a kind of thermoplastic elastomer) content and impact strength in the systems in which variable contents of EPR are added to thermo polypropylene (PP; which is also a thermoplastic resin). Fig. 11 on page 373 of the document clearly shows that the higher the EPR (which is a rubber-like component) content (wt%), the higher the Izod impact strength ($kJm^{-2}$). Thus, it is clear that an increase of EPR content results in an increase of 1zod impact strength, which is an indication of impact resistance. Fig. 4 on page 368 also illustrates a relationship between EPR content (horizontal axis) and tensile (Young's) modulus (Gsa) (vertical axis). Thus, it is clear that an increase of EPR content results in a decrease of tensile (Young's) modulus, which indicates that a higher EPR content results in a more rubber-like property. Thus, this document shows that a higher impact resistance implies that the material is more rubbery, which can be correlated to 1,2-polybutadiene and 1,4polybutadiene.

In view of the above, Applicants have amended claim 1 to recite that the curable composition of the present invention is used for preparing a cured product having a Tg of 160°C or more and a bending strength of 30 MPa or more in accordance with JIS K 6911, which is different from a rubber-like product exhibiting impact resistance as in Saito et al. In addition, since in Saito, et al., butadiene rubber is added in order to enhance impact resistance of the separator, it appears that it is not intended that a curing initiator is added together with butadiene

rubber. Thus, Applicants have added claim 26, which is dependent on claim 1 and further comprises a curing initiator, as stated above.

In view of the above, Applicants submit that the present invention is not prima facie obvious.

Further, in order to demonstrate the unexpected superiority of the present invention, Applicants submit herewith an unexecuted Declaration under 37 C.F.R. § 1.132 (the executed version will be submitted promptly after it is received).

As set forth in part 1 of the experimentation section of the Declaration, Samples (A)-(D) were submitted to demonstrate the difference in physical property between 1,2-polybutadiene and cis-1,4-polybutadiene.

From these samples, the Declarant states that it is clear that contrary to cis-1,4-polybutadiene, 1,2-polybutadiene, if it has been cured as a result of cross-linking the carbon-carbon double bonds in the side chain, becomes a cured product (having a Tg of 160°C or more and a bending strength of 30 MPa or more) having a three-dimensional network structure and does not exhibit a rubber-like property anymore.

Also, as set forth in part 2 of the experimentation section of the Declaration, Samples 1-4 were submitted in which a carbonaceous material (boron containing carbon) was incorporated:

The Declarant states that the resultant four samples were harder than such samples that did not contain a carbonaceous material (i.e., the samples in part 1 above), but the fact that the cured 1,2-polybutadiene was harder than the cured 1,4-polybutadiene remains the same.

Thus, the Declarant concludes that the present invention provides unexpectedly superior results.

Therefore, in addition to not being prima facie obvious, the present invention is also not obvious because it provides unexpectedly superior results.

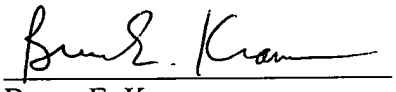
Accordingly, withdrawal of this rejection is respectfully requested.

**Conclusion**

In view of the above, reconsideration and allowance of this application are now believed to be in order, and such actions are hereby solicited. If any points remain in issue which the Examiner feels may be best resolved through a personal or telephone interview, the Examiner is kindly requested to contact the undersigned at the telephone number listed below.

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

Respectfully submitted,



Bruce E. Kramer
Registration No. 33,725

SUGHRUE MION, PLLC
Telephone: (202) 293-7060
Facsimile: (202) 293-7860

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# POLYMERIC MATERIALS ENCYCLOPEDIA

Editor-in-Chief
JOSEPH C. SALAMONE
Professor Emeritus
University of Massachusetts, Lowell

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## *Poly(butadiene-acrylonitrile)*

*See: Unsaturated Polyester Resins (Toughened with Liquid Rubber)*

## *Poly(butadiene-co-isoprene)*

*See: Rare Earth-Initiated Polymerization (of Dienes)*

# POLYBUTADIENES

Patricia Dreyfuss

Polybutadienes [9003-17-2] are obtained primarily from the interaction of 1,3-butadiene with a variety of initiators and catalysts.[1–3] The science is mature but still developing; in 1990, global demand for polybutadiene was 1,176,000 tons.[4] Currently available polybutadiene materials range from general purpose, noncrystallizing rubbers,[5–8] to highly crystalline plastics,[1,3,9] to liquid, castable resins.[10–14] The variety of polybutadiene products arises from state-of-the-art synthetic control that results in a variety of molecular architectures and a wide range of molecular weights. Differences in microstructure determine the properties of solids and liquids. Moderately high and high molecular weight polymers are solids, while low molecular weight polymers are liquids. Further modification of the resulting polymers by subsequent chemical reactions results in other useful and/or potentially useful products. The discussion that follows will be divided primarily by microstructure, but when important, polymers of different molecular weight will be discussed separately.

## MICROSTRUCTURE

When 1,3-butadiene is polymerized, the resulting polymer contains double bonds, which may exist as any one of three isomers: *cis*-1,4 [40022-03-5], *trans*-1,4 [40022-02-4] and vinyl [26160-94-5] (**Scheme I**).

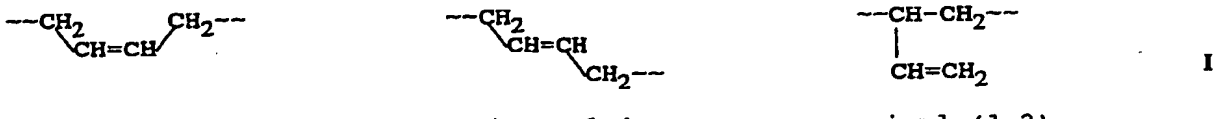
As always, the vinyl form can exist in three forms: Isotactic, in which all the side-chain vinyl groups are attached to a backbone carbon atom with the same spatial arrangement, either the D or the L isomer; Syndiotactic [31567-90-5], in which the side-chain groups are attached to backbone carbon atoms with alternating D and L configurations; and Atactic (Heterotactic) [26160-98-5], where the attachments have random D and L configurations.

Microstructure can be readily determined by IR spectroscopy[15–17] or $^1$H or $^{13}$C NMR spectroscopy.[18–21] In the infrared, the *trans*-1,4 and vinyl structures give rise to sharp bands at 965 $cm^{-1}$ and 911 $cm^{-1}$, respectively, and are thereby amenable to quantitative measurement. The *cis*-1,4 band at 725–740 $cm^{-1}$ is broader but, if necessary, can be determined by difference.

## SYNTHESIS

Polybutadienes are prepared using free radical, anionic and Ziegler–Natta initiating systems. Emulsion or solution methods of polymerization are used. The method determines the microstructure and molecular weight of the product formed. Butadiene monomer often must be purified before polymerization, and the polymerization method as well as the source of the butadiene determines the required purification technique.[1] Emulsion polymerization is largely unaffected by the impurities normally present in butadiene, but both anionic and Ziegler polymerizations are greatly affected by impurities.

Free radical polymerization of butadiene in solution gives polymers of low molecular weight, 1000–4000 g/mol [25038-44-2].[1,11] Low molecular weight polybutadiene resins originated around 1955 with the introduction of high–vinyl Buton molding compounds by Enjay Laboratories and others. ARCO Chemical Company markets a high *trans*-1,4 resin (60% *trans*-1,4, 20% *cis*-1,4, 20% vinyl).[11–13] Many of the low molecular weight commercial polybutadiene resins have terminal functional groups, including α,ω-carboxyl groups and α,ω-hydroxyl groups. Copolymeric resins with acrylonitrile have been produced.[14] Low molecular

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weight polybutadiene resins with other endgroups, such as amino and other comonomers such as styrene, have been synthesized and studied but are not commercially available.[10,11]

Free radical polymerization of butadiene in emulsion gives amorphous polymers [25038-44-2] and copolymers with high trans-1,4 content and high molecular weight. The microstructure produced depends on temperature.[1,3] Thus, polybutadiene polymerized at 50–70 °C ("hot") is about 20% *cis*-1,4, 61% *trans*-1, 4 and 19% vinyl, whereas polybutadiene polymerized at 5 °C ("cold") is about 13% *cis*-1,4, 70% *trans*-1,4 and 17% vinyl. The general features of the process have been determined.[22] Different initiators are used at different temperatures. For "cold" polymerizations, the initiator of choice is a redox system such as a ferrous salt plus an organic hydroperoxide. For "hot" polymerizations, a persulfate salt is most often used, although unusual initiators like cobalt tris(acetylacetonate) or some rhodium salts ($RhCl_3 \cdot 3H_2O$, or $Rh(NO_3)_3 \cdot 2H_2O$) also have led to high *trans*-1,4 polybutadiene polymers after emulsion polymerization.[22]

Polybutadiene rubber resulted from research done in many countries when natural rubber was in short supply during World War I and World War II. The goal was to develop a general purpose rubber that could be substituted for natural rubber. Butadiene gradually emerged as the monomer of choice because of its relatively low cost. The earliest processes were ionic. In the 1930s, Soviet chemists developed sodium rods and later finely divided sodium as the initiator of polymerization. At about the same time, German chemists discovered potassium-catalyzed butadiene polymerizations. The sodium process was used in the Soviet Union until the end of World War II, but since German chemists also discovered and developed emulsion polymerization of styrene and butadiene, polybutadiene rubber did not become important in Germany. In the United States, polybutadiene did not become an important rubber product until the introduction of solution polymerization by Phillips Petroleum in 1956 and by the Firestone Tire and Rubber Company in 1958. Alkyllithiums and alfin catalysts were introduced. The late 1950s and early 1960s brought the discovery of organometallic catalysts (Ziegler or Ziegler–Natta catalysts such as $AlEt_3 + TiCl_4$) capable of controlling microstructure, polydispersity and branching in polybutadienes prepared by solution polymerization. These catalysts often lead to polymers of very high molecular weight, and usually a transfer agent such as internal or terminal olefin (e.g., ethylene or methylallene) or hydrogen is added to control molecular weight.[1] Examples of the effects of catalyst variation on the resulting polybutadiene microstructure are shown in **Table 1**.[4] 1,2-Syndiotactic polybutadiene was the first syndiotactic polymer prepared and was reported by Natta and Corradini in 1956, very early in the history of stereospecific catalysts.[23] Ziegler and Ziegler–Natta catalysis of polybutadiene and other polymerizations has been well reviewed previously[24–26] and space does not permit a detailed discussion here. These catalysts led to the variety of polybutadienes now available. Research aimed at greater understanding and control of these processes continues.[27–32] Major producers of polybutadiene rubber include Anic, Bayer, Bunawerke Huels, Bridgestone/Firestone Tire & Rubber Company, Goodyear Tire & Rubber Company, Michelin, Phillips and Shell.[4]

**TABLE 1.** Effect of Variation of Catalyst on Resulting Polybutadiene Microstructure

| Catalyst | % *trans*-1,4 | % *cis*-1,4 | % vinyl |
|---|---|---|---|
| $Et_3Al/VCl_3$ | 97 – 98 | — | 2 – 3 |
| $Et_3Al/TiCl_4$ | 49 | 49 | 2 |
| $Et_3Al/Ti(OBu)_4$ | 0 – 10 | — | 90 |
| $Et_3Al/Cr(acac)_3$ | 18 | 12 | 70 |
| $Et_2AlCl/CoCl_2$ | 3 | 93 – 94 | 3 – 4 |

*Source:* Reference 4. With permission.

## PROPERTIES AND APPLICATIONS

As shown in **Table 2**, properties of polybutadiene vary greatly with microstructure.[4,9] With the exception of silicone rubbers, 1,4-polybutadienes have the lowest glass transition temperatures of all commercial elastomers and offer unusually good performance at temperatures at least as low as −80 °C. Polymers of randomly mixed microstructure (40–85% *cis*) are amorphous and have intermediate properties. Polymers of uniform microstructure (98–100% *cis* or *trans*) are crystalline and the melting temperature is a function of microstructure. Applications depend on properties.

### High *cis*-1,4-Polybutadiene Rubber

High *cis*-1,4-polybutadiene has useful physical properties. It crystallizes upon being stretched and thus has high tensile strength. It has excellent flexibility at low temperatures. It possesses low hysteresis, excellent dynamic properties, and outstanding resilience, tear strength and abrasion resistance. But compared to natural rubber it has low tack and green strength. There have been reports that these properties can be improved by appropriate choice of intiation systems or by slight modification of the polymer.[3] Also, the processability of polybutadiene is inferior, it has poor resistance to oil, gasoline and hydrocarbon solvents and very little resistance to heat and ozone. Solvent resistance to oxygenated solvents such as ketones is good.

High *cis*-1,4-polybutadiene has been suggested as a substitute for natural rubber in tires. Polybutadienes have unusual tolerance for high carbon black (a reinforcing filler)

TABLE 2. Selected Properties of Polybutadiene

| Property | *cis*-1,4 | *trans*-1,4 | 1,2-Isotactic | 1,2-Syndiotactic |
|---|---|---|---|---|
| Typical catalysts | Cobalt chelate $AlEt_3$ Chlorobenzene | $VCl_3$,$AlEt_3$ | $Cr(NCPh)_6$ $AlEt_3$ (Al/Cr>10) | $Cr(NCPh)_6$ $AlEt_3$ (Al/Cr=2) |
| Melting temperature, °C | (98–99%):2 | (99–100%): 97, 145[a] | (99%): 126 | 156 |
| Entropy of fusion, J/mol·K | (98%): 33.5 | (99–100%): 26.8, 11.3[a] | | |
| Heat of Fusion, kJ/mol | 2.51, 9.2 ± 0.5 | 4.184, 10.0 ± 4.2, 4.60[a] | | |
| Glass transition temperature, °C | (98–99%): −95 ("High"): −102 | −107 (94%): −83 | −15 | −15 |
| Critical surface tension of spreading, $\gamma_c$, mN/m | 32 | 31 | 25 | 25 |
| Density, mg/m$^3$ (g/cm$^3$)[b] | (98–99%): 1.01 | (99–100%): 0.97, 0.93 | (99%): 0.96 | (98%): 0.96 |
| Dielectric constant, $\epsilon$, 25 °C | | 2.51 | | |
| Loss factor, tan $\delta$ | | 0.002 (50 Hz) | | |

[a]Modifications I and II, respectively.
[b](44% *cis*-1,4, 42% *trans*-1,4, 14% vinyl) −0.895.
*Source:* Reference 4 and 9.

loadings and high oil levels.[7] Typical vulcanizate properties are shown in **Table 3**. Typically, polybutadiene tire tread stock, compared with styrene–butadiene–rubber (SBR) or natural rubber tread stock, has a lower modulus and lower tensile strength, inherently poor wet skid resistance but superior blowout resistance, equivalent or better retention of tensile strength at elevated temperature, and excellent hysteresis.

## High *trans*-1,4-Polybutadiene

High *trans*-1,4-polybutadiene is a tough crystalline elastomer with good hardness, thermoplasticity and poor hysteresis. At the highest *trans* content, the polymer is difficult to stabilize and dissolve. It has two melting temperatures that depend on the % of *trans* moiety, which in turn is determined by the catalyst system used. Table 2 shows melting temperatures of 97° and 145 °C for the 99–100% *trans* polymer, but 50° and 175 °C have been reported for a 90–99% polymer. Because of its high crystallinity, high melting temperature and difficult processing, *trans*-1,4-polybutadiene has few applications. A polymer useful as a tire rubber and processable using conventional equipment had a melting temperature of 30–40 °C, crystallized on stretching, showed 30% crystallinity by wide angle x-ray scattering analysis, and based on $^{13}C$ NMR spectroscopic analysis, had 80% *trans*-1,4, 17% *cis*-1,4, and 3% vinyl.[1,33] A blend of natural rubber, polyisoprene or SBR with > 70% *trans*-1,4-polybutadiene also has been reported to provide good tires.[3,34] Liquid *trans*-1,4-polybutadiene, a low volume specialty polybutadiene product, is used in protective coatings inside metal cans.[4]

TABLE 3. *cis*-1,4-Polybutadiene Vulcanizate Properties[a]

| Property | Value |
|---|---|
| Crosslinking, $\nu$ | $2.0 \times 10^4$ mol/cm$^3$ |
| 300% Modulus | 8.3 MPa |
| Tensile strength | 17.2 MPa |
| Elongation | 500% |
| Tensile strength at 95 °C | 9.7 MPa |
| Heat buildup | 4.4 °C |
| Resilience | 75% |
| Blowout | 120 min |
| Shore A hardness | 63 |

[a]Optimum cross-linking level using a sulfur accelerator system. Basic recipe: rubber, 100 phr; N330 carbon black, 50 phr.
*Source:* Reference 7.

## High Vinyl Polybutadienes

These 1,2 addition products consist of three main groups: syndiotactic, isotactic and atactic. High molecular weight solids and low molecular weight liquid resins are known. Each structure produces polymers with unique physical, mechanical and rheological properties.

Syndiotactic polybutadiene is a unique material that combines the properties of plastic and rubber.[1,35] Its melting temperature varies with degree of crystallinity (degree of stereoregularity and molecular weight) from about 70 °C to about 220 °C. Physical, mechanical and rheological properties are similarly affected by these parameters. It can be molded into thin films that are flexible and have high elongation. It can be blended with natural rubber and with *cis*-1,4 polybutadiene to form compatible mixtures.[1] Some physical properties of low–melting (60 – 105 °C) syndiotactic polybutadienes commercially available from Japan Synthetic Rubber Co. (JSR) are shown in **Table 4**. The modulus, tensile strength, hardness and impact strength increase with melting temperature. High-melting (190–210

**TABLE 4.** Physical Properties of Low Melting Syndiotactic 1,2-Polybutadiene

| Properties | Test method | Measured value | | | |
|---|---|---|---|---|---|
| | | JSR[a] RB805 | JSR[a] RB810 | JSR[a] RB820 | JSR[a] RB830 |
| Microstructure, % 1,2 | IR spectrum | 90 | 90 | 92 | 93 |
| Melting temperature, °C | ASTM D3418 | 59 | 71 | 95 | 105 |
| Brittle point | ASTM D746 | −42 | −40 | −37 | −35 |
| Density, g/cm$^3$ | ASTM D1505 modify (20 °C) | 0.898 | 0.901 | 0.906 | 0.909 |
| 300% modulus, MPa | ASTM D412 | 2.4 | 3.9 | 5.9 | 7.8 |
| Strength at break, MPa | ASTM D412 | 4.9 | 6.4 | 10.3 | 12.7 |
| Elongation at break, % | ASTM D412 | 800 | 750 | 700 | 670 |
| Melt flow index (150°C, 2.160 g), g/10 min | ASTM D1238 | 3 | 3 | 3 | 3 |
| Hardness | ASTM D2240 | | | | |
| Shore D | | 19 | 32 | 40 | 47 |
| Shore A | | 70 | 82 | 95 | 99 |

[a]Japan Synthetic Rubber Co.; noncrosslinked.
*Source:* Reference 1.

°C) syndiotactic polybutadiene has been the subject of a series of reviews.[36] Physical properties of highly crystalline syndiotactic polybutadiene have been reported.[37] Measurements of the mechanical properties of high-melting syndiotactic polybutadiene compared to isotactic polypropylene indicate that the former has a higher tensile strength at the breaking point, lower initial modulus and lower heat distortion temperature. In addition, syndiotactic polybutadiene can be more easily crosslinked, functionalized and cyclized. Syndiotactic polybutadiene can be easily loaded with carbon fibers and graphite. Products from 1,2-polybutadiene can be transparent, flexible and are safe for food transfer and medical use. These properties lead to applications both as a thermoplastic resin and as a rubber.[35] Applications as a thermoplastic resin include films (stretch film, laminated film, shrinkable film), footwear (primarily in soles), tubes and hoses (liquid food transfer tubes and tubes for medical practice), blow moldings, injection moldings and resin modifiers. Applications as a rubber include sponges of various kinds, footwear, solid tires, dock fenders, sporting goods, rubber gloves and other industrial goods.

High (99%) isotactic polybutadiene has been known since 1965, when Natta reported crystallographic data and other properties of the crystalline polymer.[38] Its properties have not excited sufficient interest to justify major studies or commercial development.

Atactic (amorphous) high 1,2-polybutadiene has excited considerable interest in recent years.[1] Its low hysteresis and good wet grip/rolling resistance characteristics make this polymer a potential candidate for tire tread formulations with lower tire energy loss and better fuel economy. The preparation of amorphous, high (99%) 1,2-polybutadiene was first reported in 1981.[39] Living anionic polymerization was used. Vinyl content was controlled by the choice and ratio of polar modifier to the active lithium catalyst, as well as by the polymerization temperature.[40–42] Microstructure has a marked effect on properties. **Figure 1** shows that as the vinyl content is changed from 0 to 100%, the $T_g$ of the resulting polybutadiene changes from about −100 °C to about +5 °C.[1] Effects of polymer microstructure on other

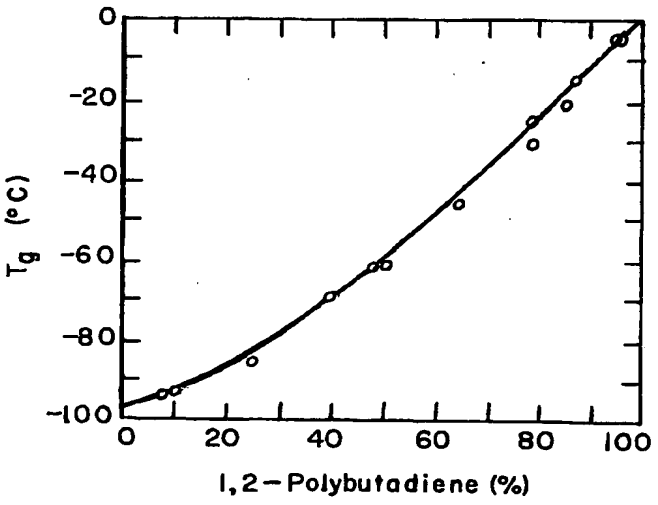


**FIGURE 1.** $T_g$ of polybutadiene as a function of 1,2 content. *Source:* Reference 1. With permission.

physical tire properties is depicted in **Figure 2.**[1] A low vinyl polybutadiene (10–30% 1,2; $-70\ °C<T_g<-85\ °C$) has good wear and excellent fuel economy but poor traction. A high vinyl (80–95% 1,2; $-10\ °C<T_g<-30\ °C$) has excellent traction and fuel economy but poor wear properties. The optimum balance of traction, wear and rolling resistance is near 70% 1,2-polybutadiene with a $T_g$ of $-40\ °C$.[1] Anionically prepared polybutadiene has the additional advantage of being readily functionalized by polar groups. Functionalization has been reported to dramatically improve polymer-filler interaction and reduce tread hysteresis.[40–42]

## Medium Vinyl Polybutadiene

Medium vinyl polybutadienes have approximately 35–55% vinyl moieties.[3] Their $T_g$s are in the range $-50$ to $-70\ °C$ and they have wear, wet-skid, heat buildup and rolling resistance properties, which are similar to those for SBR prepared by emulsion polymerization.[3] They are prepared by anionic polymerization with an added polar compound such as an ether or tertiary amine. Butyl lithium plus either 1,3-dipyrrolidine-2-propanol[43] or 2,2-*bis*(tetrahydrofuryl) propane[44,45] are examples of initiator systems. Use of medium vinyl polybutadienes in blends with natural rubber and/or SBR also has been considered (See references in (3)).

## Mixed Microstructure Polybutadiene

An amorphous polybutadiene of 10% vinyl, 35% *cis*-1,4, and 55% *trans*-1,4 structures can be made with a living anionic initiator.[1,46,47] This polymer is sold by Bridgestone/Firestone and Asahi under the names Diene 35 and Taktene, respectively. Its green strength is poor but it shows excellent physical properties, especially tread wear and low hysteresis, when compounded in a tire tread. Like other anionically initiated polymers, this one has been functionalized with ketones, aldehydes, acid chlorides and metal halides of silicon and tin. Some of these functionalized polymers may result in rubber compounds with improved properties.[1,48]

## Liquid Polybutadienes

High vinyl (>90%) liquid polybutadienes have been used to make thermosetting resins with excellent electrical properties, high thermal distortion temperatures, low water absorption and ready cure with peroxide catalysts. Solvent resistance to aromatic and aliphatic hydrocarbons is poor, but solvent resistance to oxygenated organic solvents is good. These prepolymers are cured between room temperature and about 160 °C, using a peroxide selected to decompose at the desired temperature. Near room temperature, molecular weight extension and viscosity increases occur. High temperature cures begin at about 121 °C and hard resins are produced. It is postulated that vinyl activity predominates. Care must be taken to keep curing temperatures below about 232 °C, where thermal cyclization begins and a highly crosslinked brittle material is formed. The resins generally are mixed with large amounts of fillers, and mixing takes place in dough-type equipment. Various fiber fillers, such as E-glass, S-glass, quartz and aramid (Kevlar 49) have been used to prepare structural laminates. **Table 5** shows some typical mechanical properties for a Kevlar 49–filled composite.[10]

Liquid polybutadienes with functional endgroups undergo chemical reactions typical of the functional group. For example, polybutadienes with α,ω-hydroxyl endgroups can be fabricated in polyurethanes by reaction of the diols with isocyanates or into polyesters by reaction with some acids, acid chlorides or acid anhydrides. Polybutadienes with α,ω-carboxyl groups can be chain extended and crosslinked using diepoxides. RIM processing can be used. Because of their combination of excellent electrical properties and chemical resistance, polybutadiene–based composites have been recommended for use in radome construction.[10] Polyurethanes from polybutadiene resins are used as solid fuel propellants when filled, for example with ammonium perchlorate, and for other military and aerospace uses.[11,48,49] Polyurethanes based on polybutadiene diols are notable for excellent low-temperature properties, compatibility with low-cost hydrocarbon oils, and a degree of resistance to hydrolysis claimed to be much superior to that of polyether-based or especially polyester-based polyurethanes. These properties have led to applications in electrical insulation, waterproofing membranes or coatings and

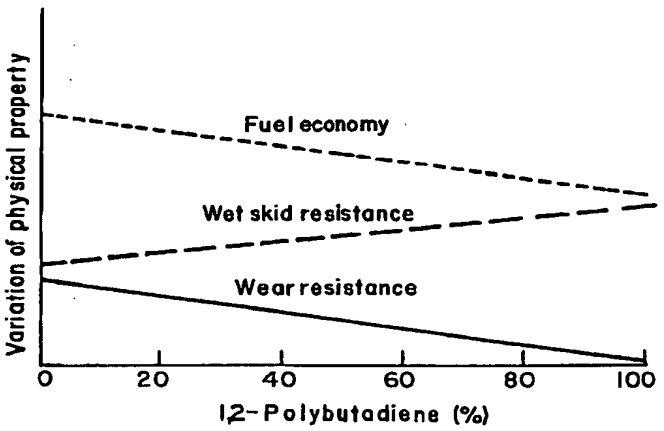


**FIGURE 2.** Effect of 1,2-polybutadiene level on tire physical properties. *Source:* Reference 1. With permission.

TABLE 5. Mechanical Properties of Unidirectional Kevlar 49 Filled Polybutadiene

| Property | Value |
|---|---|
| Flexural strength | 351 MPa |
| Flexural modulus of elasticity | 56 GPa |
| Interlamellar shear | 13.9 MPa |
| Transverse flexural strength | 13.9 MPa |
| Transverse flexural modulus of elasticity | 13.9 MPa |

[a]The polybutadiene, Dienite PM-502 from Firestone Synthetic and Latex Company, is no longer available.
*Source:* Reference 10.

liquid-castable general purpose rubber goods.[11] Chain-extended products can be used in molding compounds, caulks, mastics, joint sealers in the construction industry, coatings, adhesives, potting compounds for transformers and submersible electric motors and pumps, and thermosetting laminates.[4,11]

## Other Applications

A polybutadiene with 60% *trans*-1,4, 20% *cis*-1,4, and 20% vinyl configuration is used in the manufacture of ABS polymers.[4] Polybutadiene also is used in the manufacture of impact-modified polystyrene. Both applications capitalize on the contribution to impact strength of the low glass transition temperature of the polybutadienes selected. Some polybutadienes are used as the base polymer for other graft copolymers. Polybutadienes have been chemically modified in various ways. Hydrogenation of a polybutadiene with moderate amounts of 1,2-units gives poly(ethylene-co-butylene), whereas hydrogenation of a linear polybutadiene gives a polymer very similar to polyethylene.[51] Cyclic azo-ene modification of polybutadiene, especially modification of 1,4-polybutadienes with isopropyl azodicarboxylate, results in polymers with exceptional green strength and tack properties.[52] Chlorination of *cis*-1,4–polybutadiene leads to regular head-to-head vinyl chloride polymers.[53] Chlorination in the presence of nucleophilic reagents like tetrahydrofuran leads to a wide variety of other hitherto inaccessible copolymers.[54–56] Discussion of the preparation, properties and applications of these materials derived from polybutadiene is beyond the scope of this review. They are mentioned here to illustrate the versatility of this mature but ever-evolving polymer.

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### *Poly(1-butene)*

*See: Monomer-Isomerization Polymerization (2-Butene with Ziegler–Natta Catalysts)*
*Nylon-6 (Depolymerization)*
*Polyolefins (Overview)*

### *Poly(butylene naphthalate)*

*See: Poly(alkylene naphthalate)*

### *Poly(butylene terephthalate)*

*See: Poly(butylene terephthalate) (Annealing Behavior, Thermal Analysis)*
*Poly(butylene terephthalate)/Polycarbonate Blends*
*Spheres, Poly(butylene terephthalate)*

## POLY(BUTYLENE TEREPHTHALATE) (Annealing Behavior, Thermal Analysis)

Richard E. Robertson* and Junkyung Kim
*Macromolecular Science and Engineering Center and Department of Materials Science and Engineering*
*The University of Michigan*
Mark E. Nichols
*Ford Research Laboratory*

Scanning calorimetry has been used extensively to examine changes in the thermal behavior of polymers as a result of annealing below the melting temperature.[1] A typical thermogram, obtained from well below the annealing temperature to above the melting point, is often perplexing because of the occurrence of multiple melting peaks.

Poly(butylene terephthalate) (PBT) is a polymer that often displays multiple peaks.[2–5] Depending on its thermal history, PBT can exhibit up to three apparent melting peaks during thermal analysis. In addition, two different types of spherulites can be present: one having the usual extinction pattern when viewed between crossed polarizers, with extinction parallel with the axes of the polarizers, and the other having the extinction pattern rotated by 45°.[3,4] Because the latter unusual spherulites can be transformed to usual ones by annealing near the melting temperature, an association of these spherulites with specific melting peaks seems plausible. But the association cannot be more than partially true, because Yeh and Runt[2] found, from combined light scattering and thermal analysis studies, that the usual spherulites contribute to each endothermic peak resulting from annealing. On the other hand, an explanation for the multiplicity of endothermic peaks in terms of distinct structures is unnecessary because as many as three melting peaks can occur

*Author to whom correspondence should be addressed.

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# NISSO-PB製品紹介

基本樹脂 水素添加型PB樹脂 変性樹脂 硬化物の特性 応用製品 荷姿

## 【注型樹脂】

NOSSO-PBにラジカル重合開始剤を添加して加熱しますと発熱してゲル化し、ついには硬度の高い透明な樹脂になります。またNISSO-PBとスチレン、ジビニルベンゼン、メタクリル酸メチル、アクリル酸エチル、ジアリルフタレートのような重合性ビニルモノマーとの混合物もラジカル重合開始剤の作用で同様に硬化して樹脂となります。
NISSO-BPを実際に注型用樹脂として使用する場合には、一般に相当量のフィラーを加えますが、NISSO-PBの特長を知って戴くために、フィラーを含まない樹脂硬化物の特性を示しますと、下表の通りです。
比重が小さいこと、熱変形温度が高いこと、硬度、透明度、耐水耐薬品性、電気特性が、特に優れていることは、NISSO-PBの大きな特長です。

cured 1,2-polybutadiene resin

| 組成(重量部) | 処方番号 | No.1 | No.2 | 備考 |
|---|---|---|---|---|
| B-3000 (1,2-ポリブタジエン樹脂) | | 100 | 90 | - |
| Styrene | | - | 10 | - |
| Dicumyl Peroxide | | 2 | 2 | - |

bending strength

| 特性 | | 処方番号 | No.1 | No.2 | 備考 |
|---|---|---|---|---|---|
| 比 重 | | | 0.97 | 0.97 | 23°C ASTM D792 |
| 機械的特性 | バーコール硬度 | | 34 | 35 | 〃 D2583 |
| | 曲げ強さ(kgf/mm²) | | 3～5 | 5～6 | 〃 D790 |
| | 曲げ弾性率(kgf/mm²) | | 100～140 | 100～150 | 〃 〃 |
| | 熱変形温度(°C) | | 280°C以上 | 175 | 264psi ASTM D648 |
| 熱的特性 | 加熱減量(%) | | -0.02 | 0.02 | 180°C 24時間 |
| | 加熱減量(%) | | -0.05 | 0.08 | 180°C 240時間 |
| 吸水率 | (g/m²) | | 3.2 | 3.5 | 沸騰水中に30時間浸漬 |
| 電気的特性 | 表面固有抵抗(Ω) | | $10^{16}$～$10^{17}$ | $10^{16}$～$10^{17}$ | ASTM D257 |
| | 体積固有抵抗(Ω-cm) | | $10^{16}$～$10^{17}$ | $10^{16}$～$10^{17}$ | 〃 〃 |
| | 絶縁破壊の強さ(KV/mm) | | 44 | 40 | JISK-6911 |
| | 耐アーク性(秒) | | 130 | 115 | 〃 〃 |
| | 耐トラッキング性(滴) | | 101 | 101 | 電気学会推奨法 |
| | 誘電率(1kHz) | 25°C | 2.4 | 2.4 | ASTM D150 |
| | | 180°C | 2.4 | 2.4 | 〃 〃 |
| | 〃(100kHz) | 25°C | 2.4 | 2.4 | 〃 〃 |
| | | 180°C | 2.4 | 2.4 | 〃 〃 |
| | 誘電正接(1kHz) | 25°C | 0.002以下 | 0.002以下 | 〃 〃 |
| | | 180°C | 0.002以下 | 0.002以下 | 〃 〃 |
| | 〃(100kHz) | 25°C | 0.002以下 | 0.002以下 | 〃 〃 |
| | | 180°C | 0.002以下 | 0.002以下 | 〃 〃 |
| 耐薬品性 | 10%NaOH水溶液(g/m²) | | 0.2 | 0.2 | 60°C 6時間浸漬 |
| | 10%NaOH水溶液(〃) | | 0.1 | 0.1 | 〃 〃 |
| | 10%塩酸(〃) | | 0.1 | 0.1 | 〃 〃 |

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## MATERIAL BEHAVIOUR

# An Investigation on the Impact Fracture Characteristics of EPR Toughened Polypropylene

W.Y. Tam, T. Cheung & R.K.Y. Li

Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong

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*ABSTRACT*

*The effect of adding ethylene–propylene copolymer (EPR) into polypropylene (PP), with particular emphasis on the impact fracture characteristics, will be presented in this work. The impact fracture characterization techniques used include the notched Izod impact strength, drop-weight dart impact, and the impact fracture toughness* $G_c$. *It was observed that different impact velocity needs to be selected for the different techniques in order to ensure a well defined failure situation and to obtain a well defined impact fracture history based on the force–time curves measured during impact. Whenever there was a blunt or sharp notch present, EPR particles dispersed inside the PP matrix can play an effective role as a toughening additive. Linear elastic fracture mechanics (LEFM) approach for the measurement of the impact fracture toughness* $G_c$ *can be applied not only to the PP homopolymer, which failed in a brittle manner under a high rate of loading, but was also found to be applicable to EPR modified PP, except that plastic zone correction was required.*

## 1 INTRODUCTION

Polypropylene (PP) is extensively used in the packaging and textile industries. However, its application as an engineering thermoplastic is somewhat limited due to its relatively poor impact resistance. Impact modifiers such as ethylene–propylene copolymer (EPR) and ethylene–propylene diene copolymer (EPDM) are often added to PP in order to improve its toughness.[1-5]

The toughness of a material is usually evaluated by means of an impact test. Basically, it compares the energy absorbed by a given material during

fracture. Since the impact strength is not a fundamental material property but varies with the specimen geometry, numerous impact tests and standards have been devised to measure and compare the impact resistance of different materials: the simplest being the notched Izod and Charpy impact tests. They provide the total energy consumed during the whole impact fracture process without a detailed description of the energy consumption in each phase of the fracture process. Therefore, these methods only serve to categorise the toughness of different materials.

A more refined method for measuring the impact properties is the instrumented impact test, in which a load transducer is placed inside the striker to measure the impact force experienced by the sample during fracture. Thus, various fracture modes like crack initiation, crack propagation, crack arrests, etc. can be identified.[6]

Even though polymeric materials display viscoelasticity when tested in a tensile or oscillatory mode, they tend to fail in a brittle manner under impact due to the high loading rate exerted on the test pieces. The effect is further exaggerated by introducing a razor-sharp crack in the sample, minimising the plastic zone ahead of the crack tip and extending the application of linear elastic fracture mechanics (LEFM) to this group of materials. Thus, toughness parameters like the stress intensity factor and the critical strain energy release rate ($K_c$ and $G_c$ respectively) can be determined.[7]

Although the impact properties of impact-modified PP systems have been studied by the traditional impact testing techniques,[8-12] the impact fracture toughness and the corresponding mechanisms have received only limited attention.[5,11,12] This paper aims to investigate the impact fracture toughness and the toughening mechanisms of PP/EPR blends under various impact loading conditions. The correlation of results derived from different impact tests will also be discussed.

## 2 EXPERIMENTAL PROCEDURE

### 2.1 Materials and sample preparation

The PP homopolymer and the impact modifier (an EPR copolymer) used in this work were Pro-fax 6331 and Hi-fax RA061 respectively, and both were supplied by the Technical Centre of HIMONT (East) Limited. Blends with different PP/EPR ratios were compounded using a single screw extruder (Brabender Plasticorder 2000) at 220°C and the extrudate was subsequently pelletised. The constitution of different PP/EPR mixtures and their designations are summarised in Table 1. The volume fraction of EPR ($V_{EPR}$) in the blends were calculated according to:

$$V_{EPR} = \frac{W_{EPR}/\rho_{EPR}}{W_{EPR}/\rho_{EPR} + W_{PP}/\rho_{PP}} \quad (1)$$

where $W_{EPR}$ and $W_{PP}$ are the EPR and PP weight fraction, $\rho_{EPR}$ and $\rho_{PP}$ are the densities of EPR and PP, taken as 0.88 and 0.90 g/cm$^3$, respectively.

The blended pellets were injection moulded (Chen Hsong Mark II-C injection moulding machine) into plates with dimensions $6 \times 80 \times 150$ mm$^3$. The samples for various impact and tensile tests were cut from the plates according to the diagram shown in Fig. 1. Five bars, labelled from position (i)–(v), were yielded from each plate.

**TABLE 1**
Compositions of the PP/EPR blends used in this work

| *Designation of the blends used in this work* | *Weight % of EPR* | *Volume % of EPR* |
|---|---|---|
| PP | 0 | 0 |
| 9EPR | 9 | 8.98 |
| 17EPR | 17 | 16.6 |
| 30EPR | 30 | 29.16 |

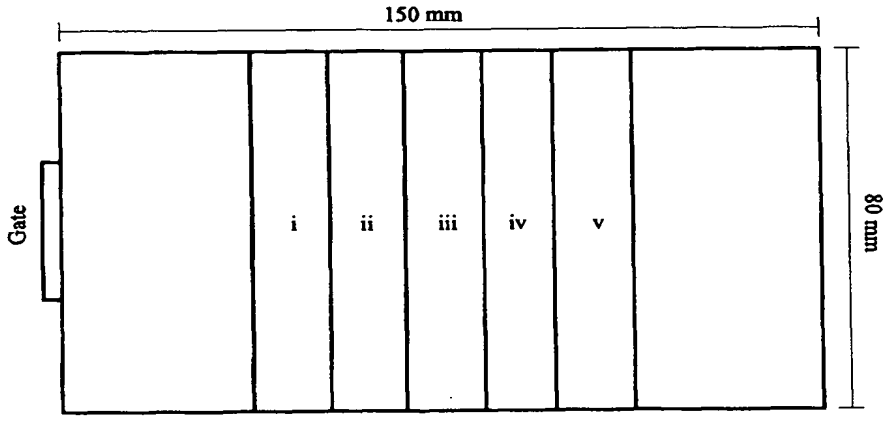


**Fig. 1.** Schematic diagram showing various cuts from the injection moulded plate. Position (i): Izod impact test; positions (ii) and (iv) tensile test and positions; (iii) and (v) Charpy impact fracture test.

### 2.2 Tensile testing

Tensile bars with a gauge width and length of 10 and 30 mm, respectively, were machined from positions (ii) and (iv) of the injection moulded plates (Fig. 1). Tensile tests were carried out using an Instron tensile machine (model 4206) under a cross-head speed of 5 mm/min. The strain was measured using an extensometer with a gauge length of 12.5 mm. The results reported for the tensile modulus, the tensile strength and the elongation at yield were averaged from five tests.

### 2.3 Impact fracture toughness ($G_c$)

Sharp notched, single-edge Charpy impact tests were carried out to measure the $G_c$ for different PP/EPR blends. They were conducted using a Ceast Fractovis instrumented drop-weight impact tester. The impact specimens, 80 × 13 × 6 mm$^3$, were obtained from positions (iii) and (v) of the injection moulded plates (Fig. 1). A schematic diagram for the Charpy impact specimen geometry is shown in Fig. 2.

The sharp notch in the sample was introduced first by sawing a slot before tapping with a fresh razor blade.[13] The exact notch length, $a$, was measured from the fractured specimen using a travelling microscope. The samples were simply supported, with a span length of 52 mm (a span-to-width ratio of four). An impact velocity of 2 m/s was used for all samples. With the presence of the sharp crack, the force (hence the energy) required to break the sample was significantly reduced. Therefore, a relatively low impact velocity was selected in order to reduce the noise, which was found to superimpose on the impact force–time curve.[14]

The impact fracture toughness, $G_c$ were calculated from:

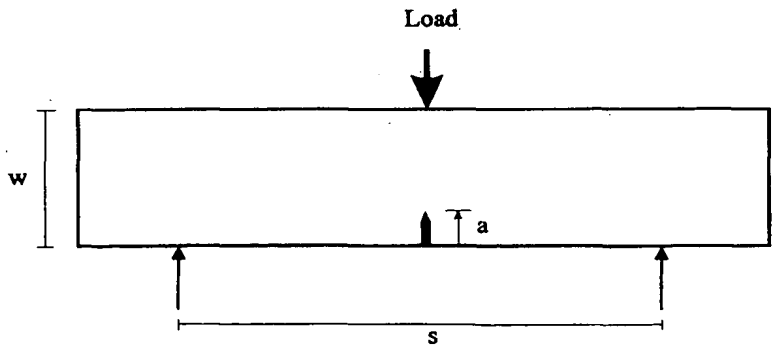


**Fig. 2.** Specimen geometry for the Charpy impact fracture test.

$$U = G_c BW\phi + E_k \quad (2)$$

where $U$ is the impact fracture energy, $B$ is the sample thickness, $W$ is the sample width, $E_k$ is the kinetic energy loss and $\phi$ is the calibration factor which depends on the ratio $a/W$. If the linear elastic fracture mechanics conditions are satisfied, $G_c$ could be calculated from the gradient of the plot of $U$ against $BW\phi$.[15]

### 2.4 Izod impact test

Notched Izod impact tests were carried out according to ASTM D256-84, using a Ceast pendulum impact tester. The samples were cut from position (i) of the injection moulded plates (Fig. 1). Five tests were conducted and the average was reported for each blend.

### 2.5 Instrumented drop-weight dart impact test

For the instrumented drop-weight dart impact tests, the injection moulded plates were cut into two equal halves, each having dimensions of 75 × 80 × 6 mm$^3$. A total of ten samples were tested for each blends. A Ceast Fractovis instrumented drop weight impact tester with a hemispherical tup (tip diameter = 20 mm) was used for the tests. The samples were fully clamped by an annular support-ring and movable clamp mechanism. The exposed surface for impact was circular in shape with a diameter of 38.1 mm. A higher impact velocity of 10 m/s (compared with 2 m/s employed for the Charpy impact test as described in Section 2.2) ensured the total penetration of the impact tup through the toughest 30EPR samples.

### 2.6 Fractography

The fractured surfaces from the Charpy impact tests were examined using a Jeol (JSM 820) scanning electron microscope (SEM). The samples were gold coated before SEM examination.

## 3 RESULTS

### 3.1 Tensile test

The tensile stress–strain curves for PP and various PP/EPR blends are compared in Fig. 3. Also included in Fig. 3 is the stress–strain curve for 100% EPR copolymer for comparison. Apart from the pure EPR copolymer, all

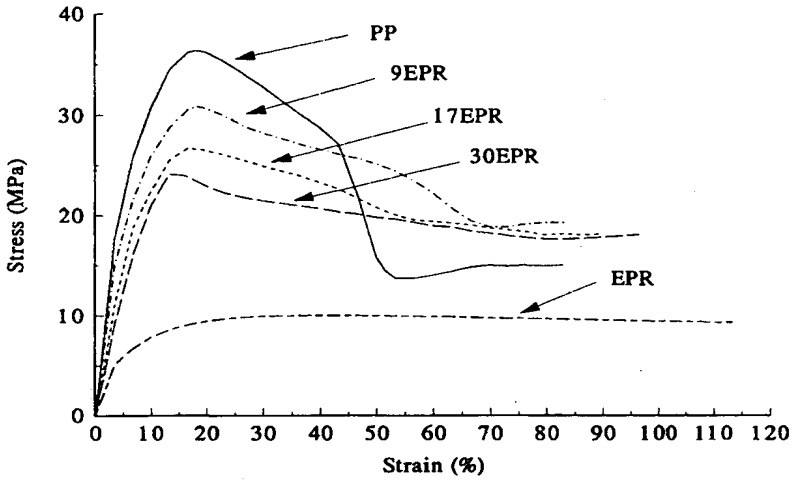


**Fig. 3.** Stress–strain curves for various PP/EPR polymer blends.

samples displayed the typical characteristic of a ductile thermoplastic, i.e. stress whitening followed by necking and drawing. Figure 4 shows the average tensile modulus and tensile strength at yield as a function of the EPR content. It clearly shows that both tensile modulus and strength at yield decreased with increasing EPR content. However, the elongation at yield did not seem to show any consistent trend with the EPR content (Fig. 5).

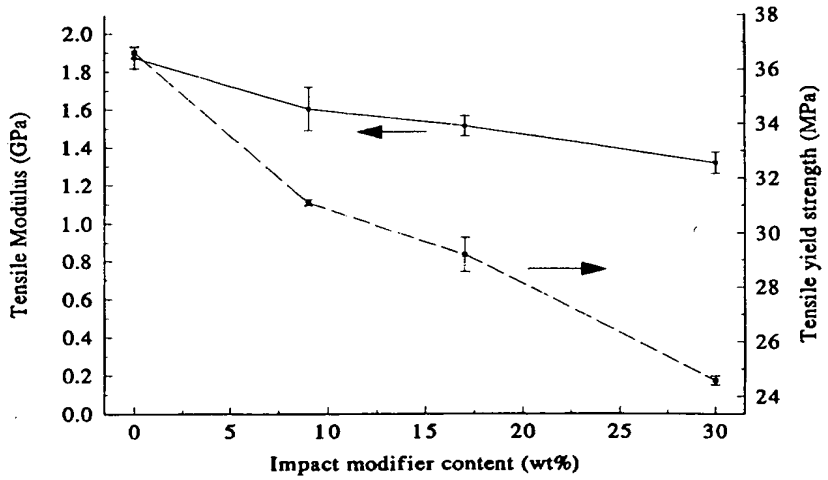


**Fig. 4.** A plot of tensile strength and Young"s modulus against EPR content.

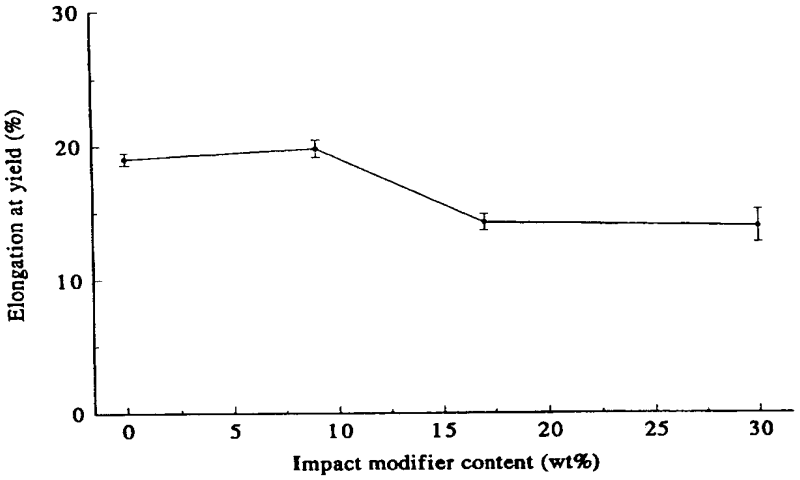


**Fig. 5.** A plot of elongation at yield against EPR content.

### 3.2 Impact fracture toughness $G_c$

The Charpy impact force–time curves for the sharp-notched PP and the PP/EPR blends are shown in Fig. 6 (the origin of each has been shifted horizontally for the reason of clarity). Secondary oscillations were seen to superimpose on all the force–time curves. For the more brittle materials, such as PP and 9EPR, the magnitudes of those oscillations were quite significant in

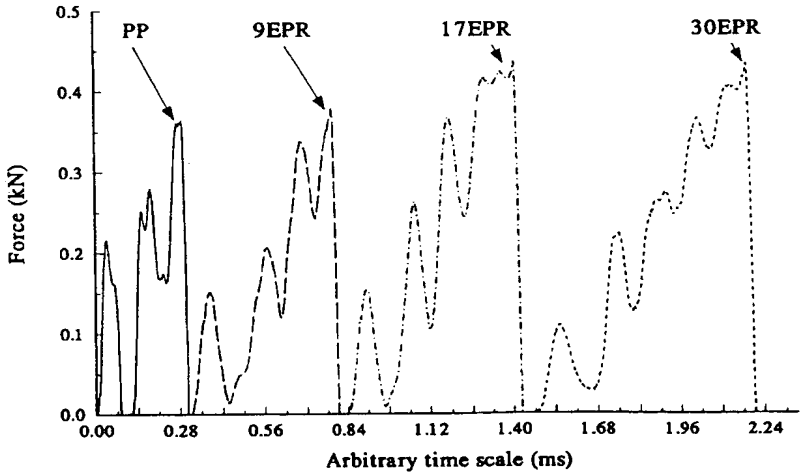


**Fig. 6.** The force–time curves of various polymer blends recorded during the Charpy impact fracture test. The origins of the 9, 17 and 30EPR have been shifted horizontally for clarity.

relation to the actual force–time histories, even though a relatively slow impact velocity of 2 m/s was used in this part of the work. Owning to the fact that the energy consumed by the sharp-notched specimens was small when compared with the energy possessed by the striker, the striker velocity was not expected to decrease significantly during the whole impact event.

It can be seen from Fig. 6 that all samples possessed a linear force–time curve up to a maximum, followed by an unstable crack propagation which is indicated by the nearly vertical drop in the force–time curve. It is expected that the fractures were either brittle or semi-brittle in nature. When the fractured surfaces were examined by eye, a stress-whitening zone was observed ahead of the notched edge. A schematic representation of the fractured surface is shown in Fig. 7.

In general, the radius of the stress-whitening zone increased with the EPR content. It was insignificant for both PP and 9EPR but measured to be 1.3 and 2 mm for 17EPR and 30EPR, respectively. This observation confirmed that the fracture was semi-brittle in nature for 17EPR and 30EPR. In order to apply the LEFM to evaluate $G_c$ for these materials, a crack tip plastic zone correction was carried out.[15] An effective crack length, $a_f$, was used to determine the calibration factor $\phi$ in eqn (2) where:

$$a_f = a + r_p \tag{3}$$

in which $a$ is the original crack length and $r_p$ is the plastic zone size. For PP and 9EPR, $r_p$ was taken as zero due to the negligible stress-whitening zone observed. In the case of 17 and 30EPR, $r_p$ was taken as 1.3 and 2 mm, respectively.

When the impact fracture energy, $U$, was plotted against $BD\phi$ for the poly-

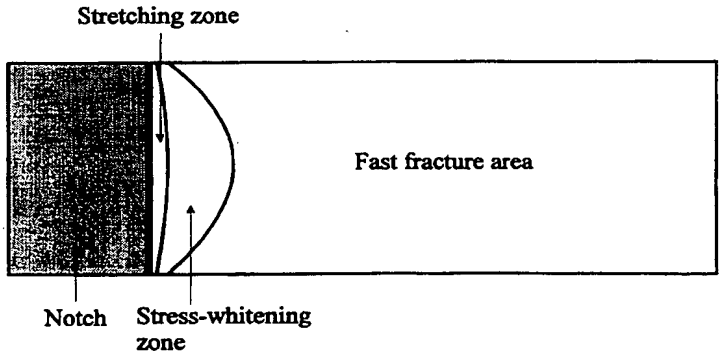


**Fig. 7.** A schematic representation of the fractured surface for the EPR modified PP.

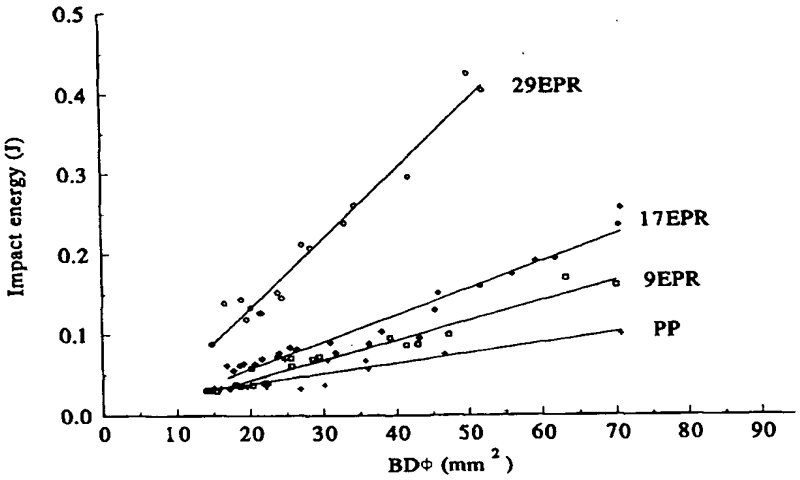


**Fig. 8.** Plots of Charpy impact energy against $BD\phi$ for various polymer blends.

mer blends, a straight line is resulted for all materials, Fig. 8. Their impact fracture toughness, $G_c$, were obtained from the slope of the plots and the results are shown in Fig. 9. Up to the 17% EPR sample, there is a gradual increase in the $G_c$ value, thereafter, a dramatic rise of approximately 250% (from the 17EPR sample) is seen in the 30EPR sample.

Figure 10(a) is a SEM micrograph of a 30EPR fractured surface, showing the area ahead of the notch tip. A higher magnification micrograph of the stress-whitening is shown in Fig. 10(b). It showed that the matrix was severely

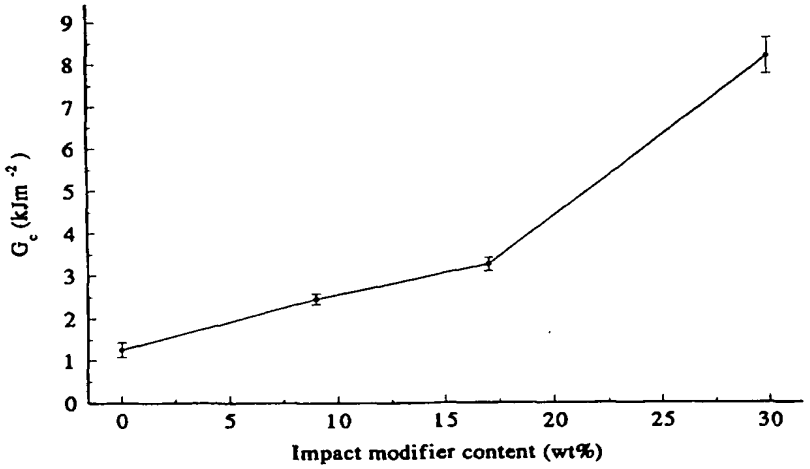


**Fig. 9.** A plot of $G_c$ against the EPR content.

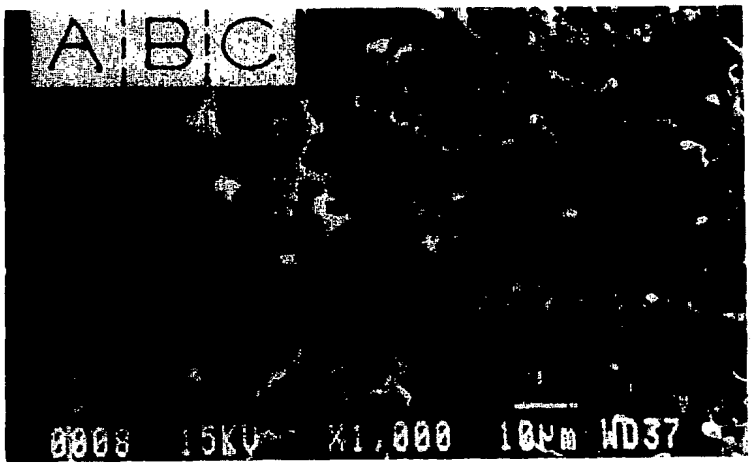


**Fig. 10.** SEM micrographs of the fractured surface for 30EPR. (a) Low magnification micrograph showing (A) the initial notch; (B) the stretching zone and (C) the stress-whitening zone.

**Fig. 10.** (b) Higher magnification micrograph of the stress-whitening zone.

damaged by cavitation, indicating that it played an important role in toughening the PP/EPR blends. In contrast, Fig. 10(c) is a micrograph of the fast fracture region with negligible matrix deformation.

### 3.3 Izod impact test

The Izod impact strength of various materials is shown in Fig. 11, the results obtained from the drop weight dart impact tests are also included for compari-

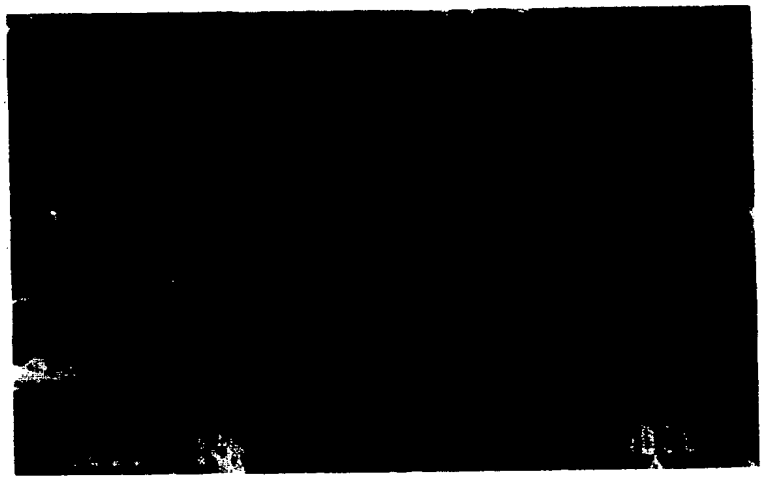

**Fig. 10.** (c) The fast fracture zone.

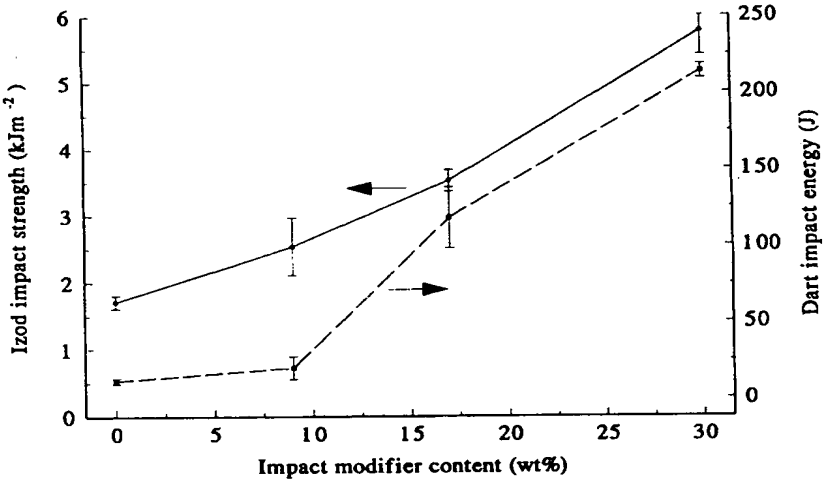


**Fig. 11.** A combined plot of the absorbed impact energy against the EPR content for the Izod and drop weight dart impact tests.

son, which will be discussed later. The addition of 9, 17 and 30 wt% of EPR had the effect of raising the Izod impact strength by approximately 48, 106 and 237%, respectively.

Figure 12 shows the area ahead of the blunt crack tip (advanced from right to left) in a 30EPR fractured specimen. Although cavitation could be observed in this region, the degree of deformation was much reduced when compared with that of the sharp crack tip in Fig. 10(a) and (b).

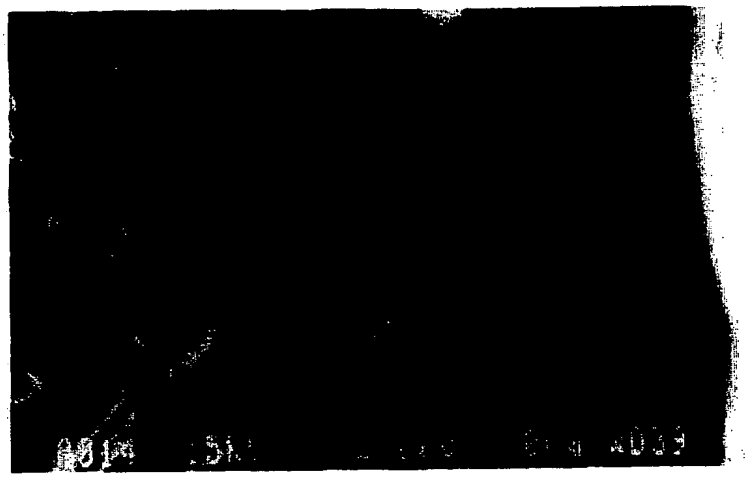

**Fig. 12.** A SEM micrograph of 30EPR showing the area ahead of the blunt crack tip resulted from the Izod impact test (the crack propagated from right to left).

### 3.4 Drop weight dart impact tests

As mentioned before, the total drop weight impact energy, $E_{total}$, taken as the area under the force–time curve, for the four polymer blends is shown in Fig. 11. Figure 13 shows typical examples of the force–time curves for the four

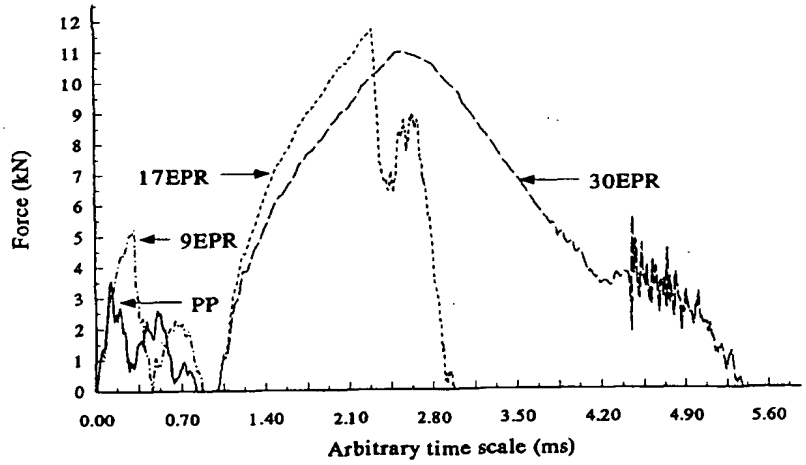


**Fig. 13.** The force–time curves of the polymer blends recorded during the drop weight dart impact test.

polymer blends and their respective fractured pieces are displayed in Fig. 14, showing the central fragments as well as the top and bottom view of the plates.

In Fig. 13, three parameters can easily be identified, they are: (a) the maximum force $F_{max}$; (b) the energy absorbed up to the maximum force, which is defined as the initiation energy $E_{init}$ and (c) the propagation energy $E_{prop}$. Therefore, the total energy absorbed, $E_{total}$, was the sum of these two energy terms. The average $F_{max}$, $E_{init}$ and $E_{prop}$ for the polymer blends are summarised in Fig. 15.

A number of common features can be identified from the force–time curves in Fig. 13. Firstly, all the curves contained two major peaks. Secondly, in the PP, 9 and 17EPR samples, a sudden drop in force was recorded immediately after the maximum ($F_{max}$), but the decrease was more gradual in 30EPR. Finally, the initial part of the curve up to $F_{max}$ was linear in PP but curved in the other EPR modified samples. The degree of curvature increased with the EPR content. The interpretation of these observations and the failure mechanism of these polymer blends will be discussed later.

Judging from the linearity in the initial part of the force–time curve and that the fractured fragments for PP were relatively free from stress-whitening (Fig. 14(a)), it is believed that it failed in a brittle manner, resulted in the lowest average $F_{max}$, $E_{init}$ and $E_{prop}$ recorded (Fig. 15). The first peak in the force–time curve is attributed to the formation and propagation of radial cracks, which penetrated beyond the boundary of the clamping ring. The second peak is related to the formation and propagation of the circumferential cracks as the striker travelled through the plate, creating a hole with a diameter of approximately 20 mm on the top surface. This circumferential crack fanned out at approximately 45° toward the underside, and eventually exited with a diameter of approximately 30 mm.

With the addition of 9 wt% EPR to PP, the initial part of the force–time curve was no longer linear (Fig. 13), an indication of plastic deformation. Furthermore, stress-whitening was observed at the tips of the central segmented fragments and in the remaining plate confined by the clamping ring (Fig. 14(b)). This evidence suggested that 9EPR failed in a semi-brittle manner. The presence of the relatively small amount of EPR had the effect of increasing the average $F_{max}$ and $E_{init}$ slightly but the $E_{prop}$ remained unaffected (Fig. 15).

For the 17EPR sample, the force–time curve clearly shows that it was plastically deformed before the initial failure (Fig. 13). Unlike the previous two examples where the central pieces have been shattered, Fig. 14(c) shows a significantly stress-whitened circular piece containing a single radial crack, which was arrested at the clamping ring boundary. The diameter of the this central piece coincided with that of the clamping ring. The high average $F_{max}$, $E_{init}$ and $E_{prop}$ indicated that 17EPR absorbed a tremendous amount of energy

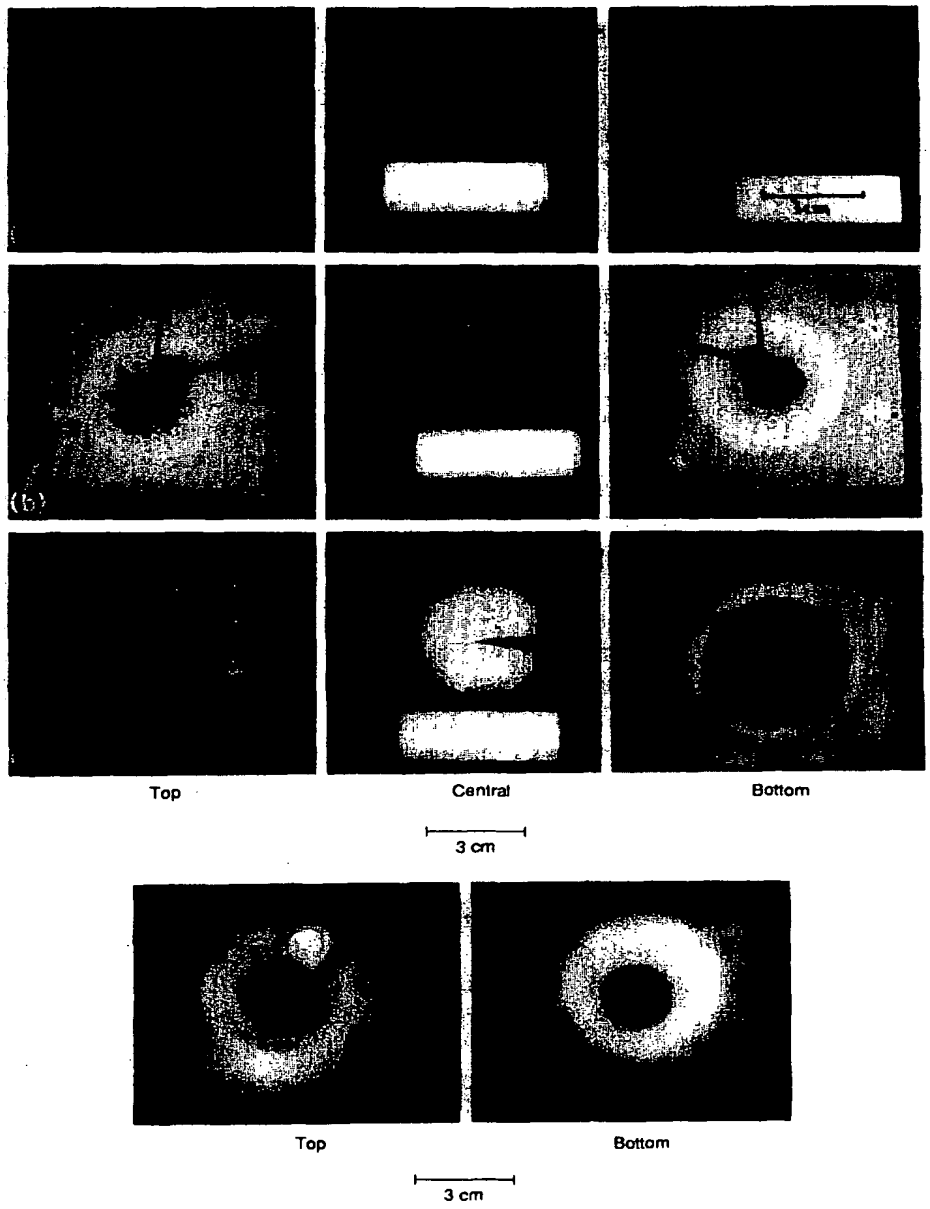


**Fig. 14.** Drop weight dart impact fractured fragments of: (a) PP; (b) 9EPR; (c) 17EPR and (d) 30EPR.

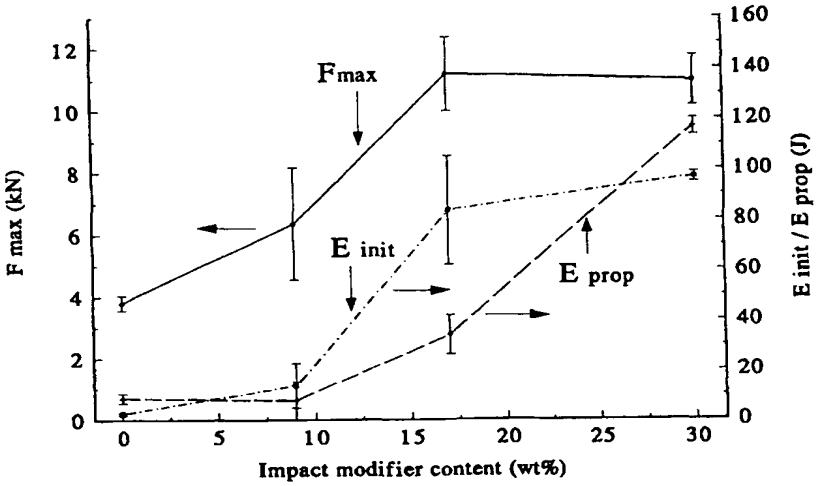


**Fig. 15.** A combined graph showing the $F_{max}$, $E_{init}$ and $E_{prop}$ against the EPR content.

(Fig. 15). The force was relieved momentarily by the formation of the radial crack, hence the sudden drop immediately after $F_{max}$. The second peak in the force–time curve is associated with the propagation of the circumferential crack around the clamping ring.

In the case of the 30EPR sample, the test plate remained in one piece after impact. A cup, in the shape of the impact tup, was drawn out of the plate. A circular tear could be seen at the tip of this cup (Fig. 14(d)).

The non-catastrophic failure highlighted the ductile nature of this polymer blend with the impacted area being stretched significantly, before the tip was partially torn away from the main body. Again, the non-linearity of the initial part of the force–time curve of 30EPR (Fig. 13) suggested plastic deformation. No fracture had occurred up on reaching $F_{max}$. Instead, the material was drawn out by the striker, slowing it down in the process. The second, rather noisy peak was associated with the tearing of the circular piece at the tip as the striker travelled through the target. Even though the average $F_{max}$ was slightly lower than its 17 wt% counterpart, its ductile behaviour rendered the highest average $E_{init}$ and $E_{prop}$ attained in the series.

## 4 DISCUSSION

With the introduction of a rubbery phase, the actual volume of the stronger and stiffer PP, and hence, the effective load bearing area of the polymer blend was reduced. Therefore, it came as no surprise that both the tensile strength

at yield and the Young's modulus decreased with an increase in the EPR content as shown in Fig. 4.

The essence of the Charpy and Izod impact test performed here was similar since they both involved the bending of a notched sample. Apart from the specimen support arrangement, the only variations between the two tests were the strain rate and the notch tip radius. According to the manufacturer's data, the velocity at impact of the pendulum striker was 3.46 m/s, similar to that of the Charpy impact velocity of 2 m/s used in this work. Therefore, the respective strain rate of the two tests employed was of the same order of magnitude. Unfortunately, the same comparison could not be carried out for the notch tip radius. The knife used for notching the Izod specimens had a tip radius of 0.25 mm but that for the razor sharp notch was unknown.

Looking at the $G_c$ values and the Izod impact strengths in Figs 9 and 11, respectively, there is a good correlation between the two results for 9 and 17EPR. However, the Izod impact strength for PP was higher than its corresponding $G_c$ by approximately 26%. The difference was assumed to be caused by the variation in the notch tip radius, where greater work was required in opening a blunt crack. It can be argued that the toughness of the EPR modified PP became insensitive to the tip radius due to the crack blunting mechanism of the EPR particles, hence the close correlation between the 9 and 17EPR samples. The large difference observed in the 30EPR sample was presumably caused by the plastic zone correction carried out in calculating $G_c$. This had the effect of lengthening the actual crack and eventually raised the $G_c$ value.

Unlike the Izod and Charpy impact tests, no extrinsic flaw was present in the dart impact test specimen. Hence, a greater amount of energy was dissipated in creating the initial failure. The introduction of the EPR particles increased $E_{total}$ by 79 979 and 1859% in 9, 17 and 30EPR, respectively. The toughening effect, in this case, was much more dramatic than that measured by Izod or Charpy impact tests.

With the aid of the force–time curves and the macrographs of the fractured pieces, the sequential event which took place during the dart impact test can be visualised here. In the case for the unmodified PP, the target plate bent under the force exerted by the striker. The high strain rate meant that it behaved elastically (linear force–time curve, Fig. 13), so that the plate failed catastrophically when it was bent beyond its elastic limit.

Moving on to the 9EPR sample, as the target plate was strained under the action of the striker, the presence of the EPR particles enabled the PP matrix to draw away, causing the stress-whitening effect as demonstrated in Fig. 14(b). This cavitation process absorbed a large amount of energy, leading to a higher $F_{max}$ and $E_{init}$ value. Similar to the previous PP example, radial cracks were seen extending beyond the clamping ring, therefore, the relatively low particle density in 9EPR had little effect in blunting and arresting the cracks, hence, there was no improvement in the $E_{prop}$ (Fig. 15).

As the EPR content is raised, the crack blunting and arresting mechanisms of the EPR particles became effective. The effect of the cavitation process was also enhanced, leading to a large increase in the $F_{max}$, $E_{init}$ and $E_{prop}$ values.

The high plasticity in the 30EPR sample caused the drop in the $F_{max}$, in analogy to the tensile strength as discussed above. Furthermore, it enabled the material to draw out, dissipating a vast amount of energy in the process, which was reflected in the large increase in the $E_{prop}$.

## 5 CONCLUSIONS

The impact properties of EPR modified PP was investigated by means of the Izod, Charpy and drop weight dart impact tests. The similarity in the testing conditions in the former two allowed their results to be compared. There was a close correlation between the two results in the 9 and 17EPR samples due to their insensitivity to the notch tip radius. The results for PP and 30EPR samples differed due to the notch tip sensitivity and the plastic zone correction, respectively. In the dart impact test, cavitation was mainly responsible for the improved toughness in the 9EPR sample. However, as the EPR content increased, the crack blunting and arresting mechanisms became effective, in conjunction with the cavitation process.

## ACKNOWLEDGEMENT

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